

The crest of Brown University is depicted. At the top, a banner curves across the frame with the word "BROWN" in the center, the number "17" on the left, and "64" on the right. Below the banner is a sun with a human-like face, rising over a range of mountains. The central element is a shield divided into four quadrants by a cross. Each quadrant contains an open book. The top-left book is labeled "1636", the top-right "1646", the bottom-left "1656", and the bottom-right "1666". At the base of the shield, another banner curves across with the Latin motto "IN DEO SPERAMUS".

Division of Engineering BROWN UNIVERSITY PROVIDENCE, R. I.

FIELD ION MICROSCOPY,^{20m, 20} OF CARBIDES OF TUNGSTEN FORMED EXTERNALLY AND IN-SITU

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American Iron and Steel Institute
Contract Grant 200

Advanced Research Projects Agency
Department of Defense
Contract SD-86
Materials Research Program

20060118003

AISI 200/2
 ARPA E61

October 1968

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ARRA-E-61

Field Ion Microscopy of Carbides of Tungsten
Formed Externally and In-Situ^{*}

by

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Abstract

The field ion images of carbides of tungsten produced by in-situ and external carburization processes are compared for the compounds W_2C and WC . In both cases it is found that the ion images are identical and that they correspond to the crystal structure normally associated with the bulk forms of these two compounds.

* Supported by the American Iron and Steel Institute and the Advanced Research Projects Agency.

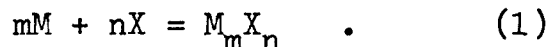
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Introduction

The field ion microscope can be a source of much significant information regarding the formation and structure of compounds of metals of the type M_mX_n which can be formed by a chemical reaction of the type



That the technique is particularly well-suited to the study of interstitial compounds formed in-situ has been illustrated by previous work^(1,2). Therefore, rather than go into great detail, we shall only briefly describe and compare the advantages of in-situ as opposed to external compound formation.

In-situ preparation involves the formation of the compound on a well-characterized and well-imaged tip of the base metal. The element X is applied to the tip by vapor deposition and diffusion is allowed to occur so that the X atoms can migrate into the bulk volume of the emitter tip. Subsequent field evaporation and field ionization can reveal the movement of the interface between compound and base-metal in three dimensions. The nature of the interface, i.e. its degree of coherency, the associated strain fields or dislocations, and the relative orientations of compound and metal on either side of the interface can all be studied using this technique.

There are, however, problems inherent in the in-situ technique of compound formation. Chief amongst these is the question as to whether the compounds thus formed are the same as the compounds

formed in the bulk. This is analogous to the problem in electron transmission microscopy where specimens thinned from the bulk material after a certain thermal or mechanical treatment differ in structure from those samples subjected to the same treatment subsequent to the specimen preparation process (i.e. specimens treated in the as-thinned condition). It was with the intention of confirming or rejecting any such discrepancy between the compound formed in the bulk and that formed by the in-situ process that this study was undertaken. This paper, then, describes a comparative study of in-situ and externally formed carbides of tungsten.

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Procedure

The field ion microscopes used in this study are of the glass construction described previously⁽²⁾. They were operated at liquid nitrogen temperature and at an ultimate vacuum of about 10^{-7} torr.

The in-situ carburization was performed in the microscope tube shown in Fig. 1. The carbon electrodes (L) are made of spectroscopic grade carbon and pointed to provide as efficient a source of carbon with as little heat radiation as possible. Once the tungsten specimen is imaged and the proper end form is established by field evaporation, the helium imaging gas is removed from the system, the field is lowered, and the carbon electrodes are rotated by means of the eccentric mounting arm to a position directly below the emitter. The tip is heated to approximately 1000°C by resistive heating of the heavier tungsten support loop and the carbon source is activated by the application of an external voltage.

At this temperature, the carbon diffuses into the tungsten to a depth equal to the radius of the tip in just a few minutes. After carburization, the specimen is returned to 77°K , the imaging gas restored, and the field is applied once again. The tip has, then, the profile shown in Fig. 2 where the carbon and carbides exist as layers. If such a tip is imaged, the initial structure will be that of the carbides and field evaporation must be employed to get down through the layers to the base metal. It should be mentioned here that this same sequence of field ion micrographs

may be examined in reverse to study the progression of carbon migration into the tungsten and to observe the formation of the various carbides.

Carbides of tungsten were formed in the bulk by heating tungsten wires resistively in an atmosphere of methane and hydrogen as shown in Fig. 3. This is a very simple apparatus and the use of heavy tungsten loops precludes any interdiffusion between the specimen wire and the supports. An autotransformer provides the necessary heating voltage and the temperatures can be measured with a suitably calibrated micro-optical pyrometer. By controlling the voltage applied to the wire, the gas mixture, and the time at temperature, varying degrees of carburization can be achieved. The resulting solid solutions and compounds may be considered representative of bulk material because of the 0.005 inch diameter wire used here.

It must be emphasized here that those wires carburized externally are suitable for subsequent preparation into field ion specimens only if they are through-carburized. It is the center of the wire that forms the apex of the field ion emitter and not the gross periphery (Fig. 2). If the times are not sufficiently long nor the temperatures sufficiently high, the center of the wire will be pure tungsten and the resulting field ion specimen and ion image will only too tragically be that of tungsten and not the compounds. Presently available diffusion data lists values of the activation energy of diffusion of carbon in tungsten but not of carbon in WC or in W_2C -- which have been found to be the rate limiting steps.

By following the voltage-current relationship during the external carburization process, it is possible to observe the change in compounds and to compute rough values of the activation energy for diffusion -- a topic which will be discussed in detail in a subsequent report.

A two-layer technique of electropolishing was used for the preparation of carbide field ion specimens. A mixture of 5 gm of NaOH and 5 gm of WO_3 in 100 ml of H_2O was floated on top of a bath of carbon tetrachloride. Polishing occurs at the interface between the layers when 15v dc is applied. Since the carbide wires are extremely brittle, spot welding of the tips to the support loops was precluded and instead, a clamp developed by Sproul⁽³⁾ was used. This is shown in Fig. 4. While the use of such a clamp prohibits resistive heating, this was not a serious handicap since the thermal treatments had already been applied to the specimens before electrolytic preparation.

Results and Discussion

Carbon is only slightly soluble in tungsten as is indicated by the tungsten-carbon phase diagram (Fig. 5). The solubility of carbon in solid tungsten has been measured at less than 0.3 atomic percent by Goldschmidt and Brandt⁽⁵⁾. The compounds of interest in this study are the W_2C and WC (the alpha form), but before examining the structures of the carbides, let us discuss the ion images resulting from the solid solution of carbon in tungsten -- however small it may be.

Despite the small solubility limit quoted above, the presence of the high field-induced hydrostatic tension must allow more carbon to dissolve in the tungsten lattice -- with less disruption or tetragonality than might be computed on the basis of field-free calculations and hard-sphere approximations. Earlier work by Machlin⁽⁶⁾, confirmed by French and Richman⁽¹⁾, proved that the ion image of the solid solution is similar to that of pure, undistorted tungsten, and that the carbon atoms do not image. The field ion micrograph of Fig. 6 contains in the center a region of either pure tungsten or the tungsten-carbon solid solution. Around the periphery of the imaging region is the mottled ion image characteristic of W_2C .

When in-situ carburization is complete, the carbide W_2C images as shown in Fig. 7a. Is this, however, the same W_2C as would have been formed by external carburization? This same sample can be removed from the field ion microscope and subjected

to electron diffraction and dark-field electron microscopy. The resulting electron diffraction pattern⁽¹⁾ corresponds to the bulk crystal structure of the compound W_2C^* . A stereographic projection based on this bulk crystal structure has been computed using the method of Sproul and Richman⁽⁸⁾ as shown in Fig. 7b and this can be used to index the field ion micrograph of an externally carburized sample of W_2C (Fig. 7c).

The compound WC produces the ion image shown in Fig. 8a. This image is hexagonally symmetrical and has been identified as WC by comparison with a stereographic projection computed on the basis of the bulk crystal structure^{**} (Fig. 8b) and by examining local atomic arrangements on certain planes such as the $(2\bar{1}12)$ ⁽¹⁾. This structure resembles very closely the field ion micrographs of WC produced externally by Meakin⁽⁹⁾. It was impossible to obtain electron diffraction patterns because the WC formed in-situ persisted for less than ten atomic layers. The ability of a compound or structure to exist in its bulk configuration when only a few atomic layers thick has been confirmed by Southon⁽¹⁰⁾ who has observed the growth of molybdenum layers on well imaged tips of other metals and reports that the characteristic molybdenum structure can be observed after only three atom layers have been deposited.

* W_2C has the CdI_2 structure. It is hexagonal close-packed with carbon at the $1/3, 2/3, 1/4$ and $2/3, 1/3, 3/4$ positions. $a=2.98\text{\AA}$ and $c=4.71\text{\AA}$.

** WC consists of two interpenetrating hexagonal lattices, one of tungsten, the other of carbon. $a=2.90\text{\AA}$ and $c=2.83\text{\AA}$.

The ion images of the compounds are not very good as field ion images go. They do have sufficient information to allow them to be indexed. There has been speculation on the lack of image points in the ion images of compounds, but the most likely explanation seems to be that of environment. Those tungsten atoms are imaged which have certain carbon neighbors. The possibility of orbitals being established between the metal and the carbon atoms or of superexchange through the carbons remains the most promising explanation. This also is being investigated by several groups at the present time and it is hoped that more can be said of this in a later paper.

Conclusions

The compounds of tungsten and carbon formed by in-situ carburization have been determined to be identical to those formed by external carburization of the bulk tungsten wire and subsequent preparation into field ion microscope specimens. Both of these methods of carbide synthesis give rise to ion images which can be interpreted on the basis of the bulk crystal structure of the compounds.

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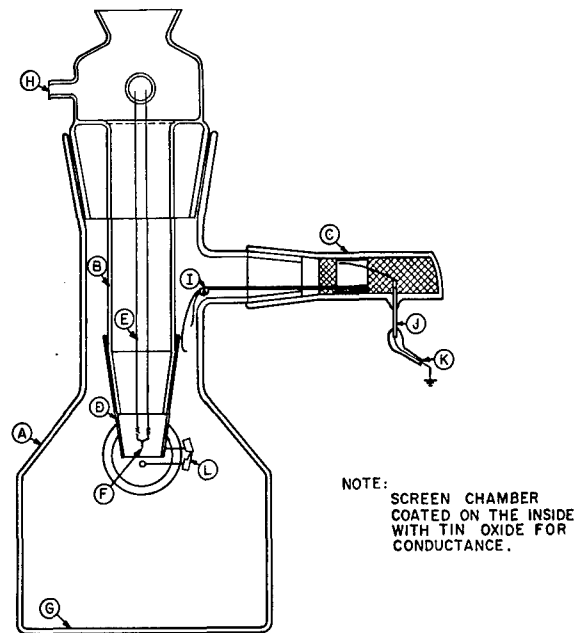


Fig. 1 Field Ion Microscope Tube for
In-Situ Carburization.

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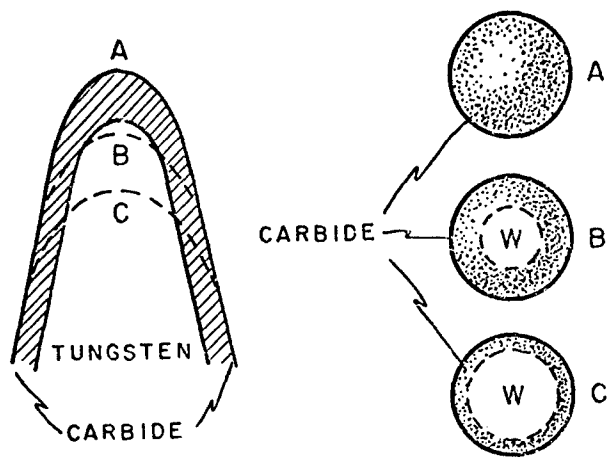


Fig. 2 Profile of Carburized Tip.

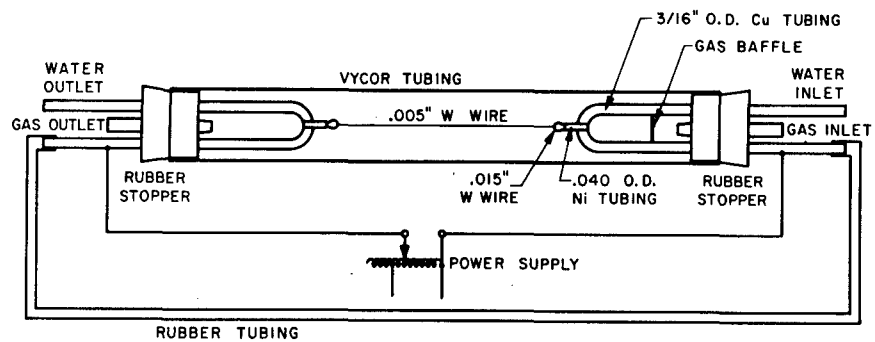


Fig. 3 External Carburization Apparatus.

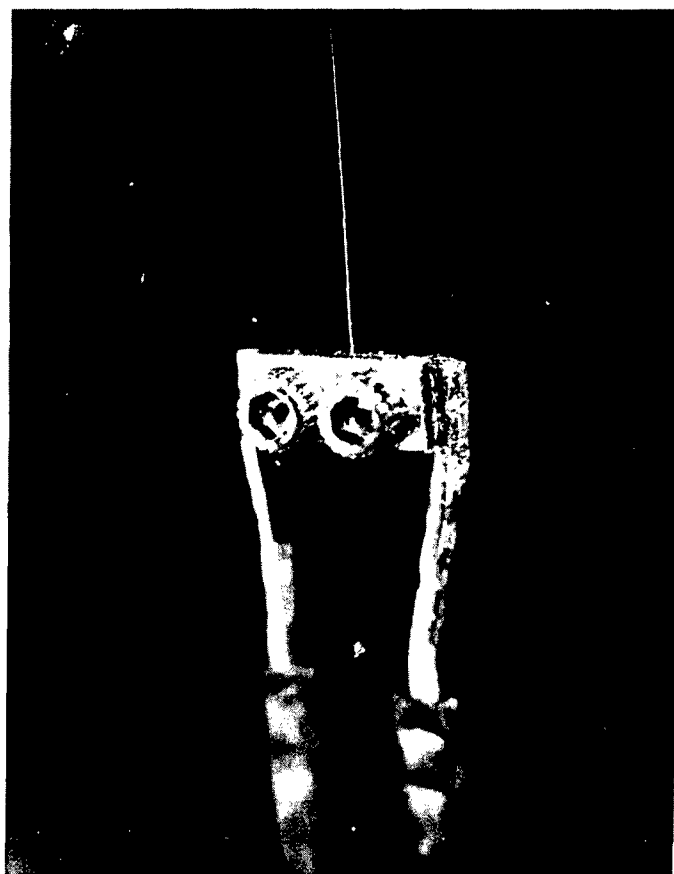


Fig. 4 Clamp for Holding Carbide Tips.

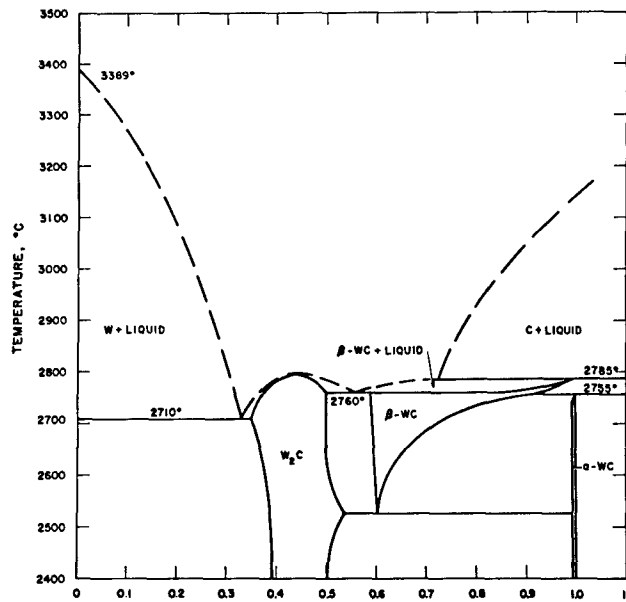


Fig. 5 Tungsten-Carbon Phase Diagram
after Doloff and Sara⁽⁴⁾.

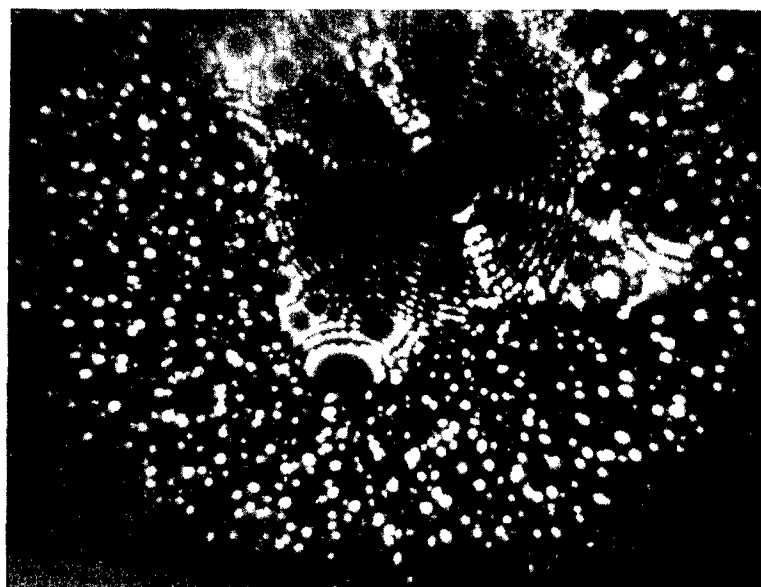
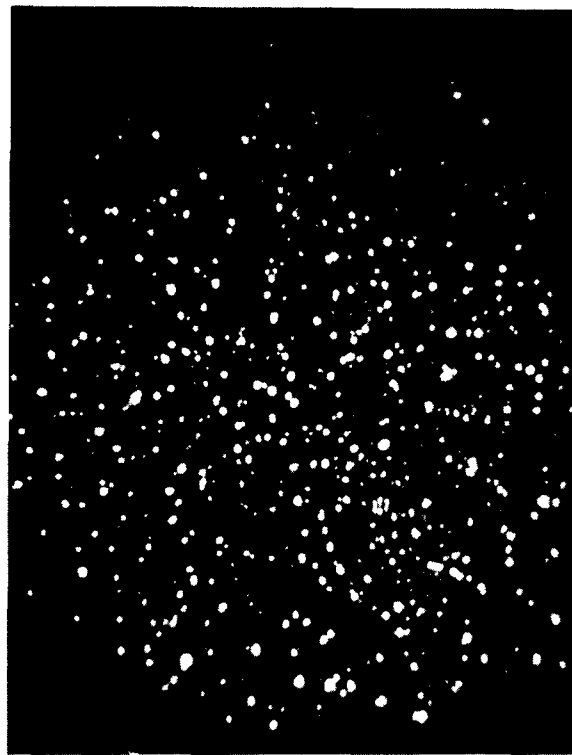
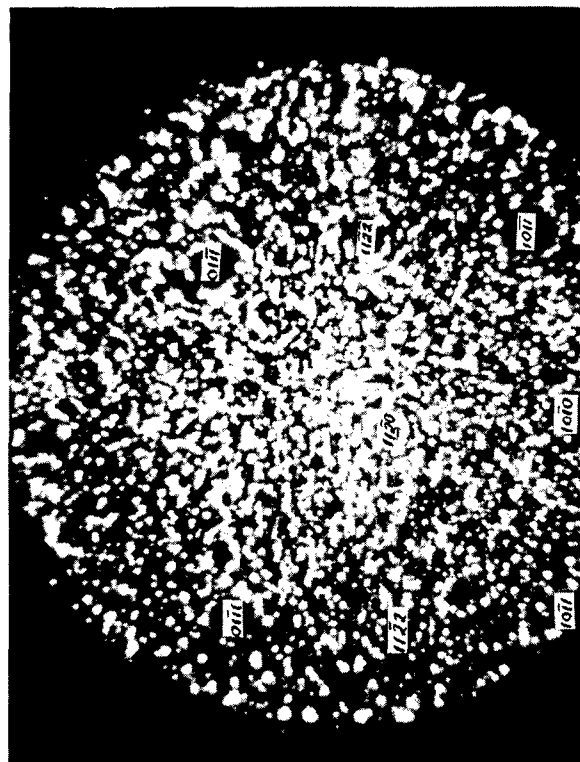


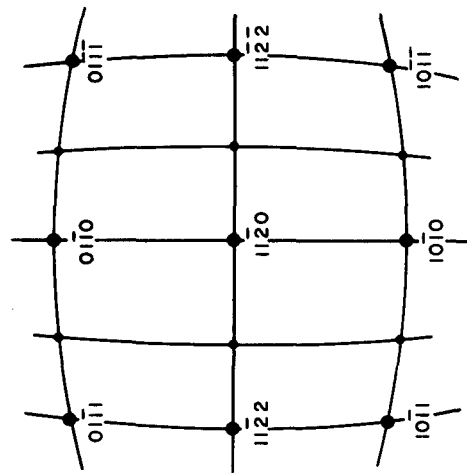
Fig. 6 Field Ion Image of Solid Solution
of Carbon in Tungsten (center) and
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(a) Formed in-situ.

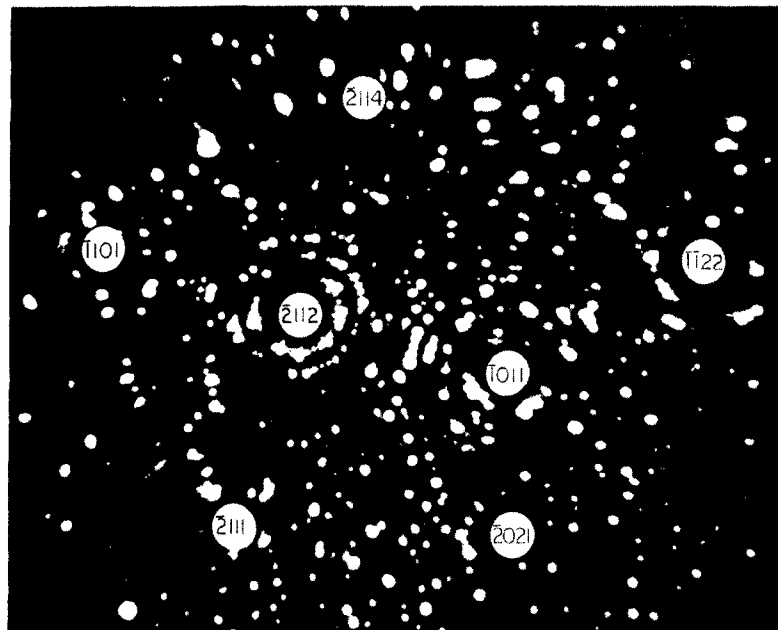


(b) Formed externally.

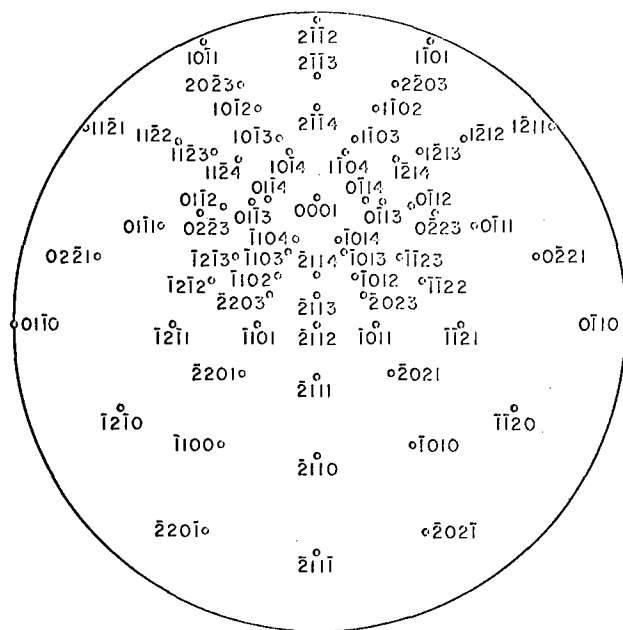


(c) Partial $(11\bar{2}0)$ Projection.

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(a) Formed in-situ.



(b) Stereographic Projection.

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